## Thermochemical Degradation Mechanisms for Reinforced Carbon/Carbon Panels on the Space Shuttle

The wing leading edge and nose cone of the space shuttle are fabricated from a reinforced carbon/carbon material (RCC). This material attains its durability from a diffusion coating of silicon carbide (SiC) and a glass sealant (ref. 1). During reentry, this material is subjected to an oxidizing high-temperature environment. Joint work between the Ohio State University and the NASA Lewis Research Center led to a survey of potential degradation mechanisms of the reinforced carbon/carbon (RCC) material at high temperatures (ref. 2).

These mechanisms include oxidation of the SiC to form a silica scale (SiO2), reaction of the SiC with SiO2 to generate gaseous products, viscous flow of the glass, vaporization of the glass, and salt-induced (NaCl) corrosion, which may lead to pinholes. Continued thermal oxidation of the SiC coating occurs as

$$SiC(s) + O_2(g) 
ightharpoonup SiO_2(s) + CO(g)$$

This adds silica to the glass coating and slows the oxidation rate. Under the extreme conditions of very low oxygen partial pressures and high temperatures, active oxidation may occur leading to SiO(g) instead of SiO2(s) and rapid material consumption.

The reaction of SiC and SiO2 occurs as follows:

$$SiC(s) + SiO_9(s) \iff 3SiO(g) + CO(g)$$

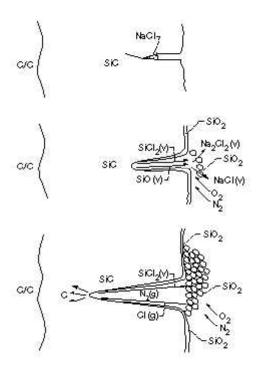
This leads to gas formation at the SiC/SiO2 interface. Total vapor pressure calculations for carbon-rich SiC, silicon-rich SiC, and SiC, which forms SiO and CO in the 3-to-1 ratio of the above reaction, indicate that it is very desirable to keep the SiC silicon-rich to minimize this gas generation. This is currently done with the reinforced carbon/carbon material on the space shuttle.

Degradation of the glass sealant was also discussed. This is primarily a sodium silicate glass. At elevated temperatures, the glass sealant flows. This is beneficial since the sealant fills the cracks in the SiC that were formed because of the thermal expansion mismatch between the SiC and the carbon/carbon. However, under extreme conditions the glass may be blown off the surface by viscous drag, exposing the SiC and possibly the carbon/carbon to attack. The sodium component of the glass also vaporizes preferentially. This is suppressed to some degree by the oxygen in the reentry environment.

After many missions, the leading-edge wing surfaces have exhibited small pinholes. A mechanism based on NaCl deposits is proposed to explain this. Before launch, the shuttle is exposed to the sea-salt-laden air of Florida for periods of up to a month. This salt can

deposit in the cracks and crevices of the reinforced carbon/carbon material on the wings and is likely to remain trapped there during launch and reentry. A cyclical chlorination/oxidation mechanism, which was proposed to explain this, is shown schematically in the figure. The trapped NaCl releases chlorine, which forms SiCl2(g) with the SiC. This SiCl2(g) migrates to the top of the pinhole and oxidizes to form SiO2. This reaction leads to the silica fume observed near the top of the pinhole and releases chlorine that returns to the silicon carbide and forms more SiCl2(g). Thus the pinhole grows. Diffusion calculations give results consistent with the observed pinhole depths.

Current work focuses on further verification of this mechanism and prediction of damage to the carbon/carbon after a pinhole is formed.



Schematic representation of chloridation/oxidation reaction mechanism. Top: Contamination of surface cracks. Center: Transient passive reaction in a pinhole. Bottom: Steady-state active reaction with pinhole growth and fume deposition at external surface.

## References

1. Williams, S.D., et al.: Ablation Analysis of the Shuttle Orbiter Oxidation Protected Reinforced Carbon-Carbon. AIAA Paper 94-2084, 1994.

2. Jacobson, N.S.; and Rapp, R.A.: Thermochemical Degradation Mechanisms for the Reinforced Carbon/Carbon Panels on the Space Shuttle. NASA TM-106793, 1995.